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Blanket and patterned growth of CdTe on (211)Si substrates by metal-organic vapor phase epitaxy

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Metalorganic vapor phase epitaxy (MOVPE) of (211)B CdTe on (211)Si using intermediate Ge and ZnTe layers has been achieved for use as substrates for the growth of HgCdTe infrared detector materials. The best (211)B CdTe films grown in this study display a low X-ray diffraction (XRD) rocking-curve full-width-at-half-maximum (FWHM) of 64 arcs for a 12 μm thick layer and Everson etch pit density (EPD) of $3x10^5$ cm^{-2}. In order to reduce the threading dislocation density further, growth on patterned layer has been investigated using Si_3N_4 as the mask. In order to achieve selective nucleation on patterned layer, process parameters were first developed. A circular pattern was used to study the anisotropy during growth and to identify the optimum orientation for parallel stripe growth windows. The optimum growth window was then used for the growth of completely merged layers.

1 Introduction

Mercury cadmium telluride ($Hg_{1-x}Cd_xTe$) is the material of choice for high performance infrared focal plane array (FPA) systems used in military applications. Epitaxial growth of $Hg_{1-x}Cd_xTe$ can be conducted on lattice-matched $Cd_{1-x}Zn_xTe$ substrates. However, there are several advantages to using Si instead of $Cd_{1-x}Zn_xTe$ substrates – lower cost, larger substrate sizes and no thermal mismatch with the read-out electronics substrate (also Si) in FPAs [1]. The chief challenge with using Si substrates for $Hg_{1-x}Cd_xTe$ epitaxy is a 19% lattice mismatch between Si and $Hg_{1-x}Cd_xTe$. This causes misfit dislocations at the interface and threading dislocations (TDs) at the surface of the $Hg_{1-x}Cd_xTe$ device layer. The TDs act as recombination centers and reduce the minority carrier lifetime. Thick (8 μm to 15 μm) CdTe buffer layers are generally used during hetero-epitaxy of $Hg_{1-x}Cd_xTe$ on Si in order to reduce the TD density. (211)B is the preferred orientation for molecular beam epitaxy (MBE) of $Hg_{1-x}Cd_xTe$ [2]. Hence there is a requirement for high-quality (211)B CdTe buffer layers on Si.

MBE has been the most widely used technique for growth of (211)B CdTe on Si. The etch pit density (EPD) produced using an Everson etch is commonly used to estimate the TD density in (211)B CdTe layers [3]. High-quality thick (~10 μm) (211)B CdTe/Si buffer layers with EPD in the mid-10^5 cm^{-2} to low-10^6 cm^{-2} range have been reported using MBE [4, 5]. For fabricating long-wavelength infrared (LWIR) $Hg_{1-x}Cd_xTe$ photo-diodes, further reduction in TD density of the (211)B CdTe/Si buffer layers is required. MOVPE may offer some advantages over MBE in this respect and hence investigated in this study.

We first investigated the growth of (211)B CdTe on blanket (211)Si substrate by metalorganic vapor phase epitaxy. It is shown that layers comparable in quality to those grown by MBE can be grown on (211)Si substrates using Ge and ZnTe interfacial layers. Once this is achieved, further reduction of threading dislocation density was attempted by using patterned growth technique also called epitaxial lateral overgrowth (ELO) technique since MOVPE growth process is more suitable than MBE for the

ELO process. The ELO technique has been successfully used to reduce the TD density in lattice mismatched hetero-epitaxial systems like GaAs/Si [6, 7], GaN/6H-SiC [8], ZnSe/GaAs [9].

2 Experimental procedure

The CdTe films were grown in a low-pressure vertical cold-wall reactor equipped with a rotating heater/substrate-holder. The starting substrates were 3" Si wafers - (112) off 3^o towards [1 1 $\bar{1}$]. These were degreased using organic solvents, followed by a RCA clean [10]. The substrates were then loaded into the reactor and heated up to the Ge growth temperature (525 °C) in hydrogen (H_2) flow. Tertiary butyl arsine (TBAs) was used to provide an As over-pressure, enabling As-passivation of the starting Si substrate. Dilute germane gas (1% GeH_4 in H_2) was used as the precursor to first grow a thin (~300 nm) Ge film. After Ge growth, the substrates were cooled down to the ZnTe growth temperature (350 ^{o}C) in the presence of TBAs. A thin (~200 nm) ZnTe film was grown using diethylzinc (DEZn) and diisopropyltelluride (DIPTe), followed by growth of thicker CdTe film (also at 350 °C) using dimethylcadmium (DMCd) and DIPTe. The CdTe growth was interrupted at regular intervals for anneal cycles, the details of the cyclic anneal procedure are reported elsewhere [11].

For studying the efficacy of using patterned growth for defect reduction, the starting substrates were ~10 µm thick MBE grown (211)B CdTe films grown on Si substrates (using intermediate ZnTe layer) provided by Night Vision and Electronic Sensors Directorate (NVESD). The substrates were of high crystalline quality; with (422) X-ray diffraction (XRD) rocking curve full-width-at-half-maximum (FWHM) less than 100 arcs and Everson EPD in the low-10^6 cm^{-2} range. Si_3N_4 was used as the mask in this study [12]. Plasma enhanced chemical vapor deposition (PECVD) was used to deposit a 200 nm thick Si_3N_4 on the CdTe layer, the Si_3N_4 was then patterned using conventional photolithography and reactive ion etching (RIE) to expose seed windows. The pattern consisted of 2 µm growth windows separated by mask widths of 38 µm. The mask deposition and patterning was conducted by Prof. Schetzina and co-workers at North Carolina State University (NCSU). CdTe growth by MOVPE was conducted as above except that the growth takes place directly on the patterned CdTe/Si wafers and used diethyltelluride (DETe) instead of DiPTe as the Te source since DETe is found to be a better source for growth at higher temperature. The key step in the process is selective nucleation i.e. the growth process parameters are chosen such that CdTe nucleation occurs in the exposed seed windows but not on the Si_3N_4 mask. After the CdTe layer becomes thicker than the Si_3N_4 film, the CdTe growth progresses in the vertical direction, as well as in the lateral direction over the mask. If the growth process is extended for a long enough time, the growth stripes from adjacent seed windows merge to form a continuous film. The main advantage of this process is that dislocations can thread from the substrate into the epitaxial layer only through the narrow seed windows, so the film that grows laterally over the mask will have a much lower threading dislocation density compared with the starting substrate.

3 Results and discussion

3.1 Growth of MOVPE CdTe on blanket (211)Si substrates One of the challenges with using Si starting substrates in a MOVPE reactor used to grow CdTe is that Si is very reactive with any trace amounts of Te present in the reactor. Severe surface degradation of the Si substrates has been observed during pre-growth temperature ramp-up [11]. This problem has been solved by using a TBAs mole fraction of ~ $4x10^{-4}$ during the temperature ramp-up and temperature stabilization steps. TBAs decomposes and the resulting As passivates the Si surface and prevents surface degradation. Even though direct growth of single crystal CdTe on (211)Si using As passivation is possible, use of Ge and ZnTe interfacial layer enable a gradual grading of the lattice constant from Si (5.431 Å) to Ge (5.646 Å) to ZnTe (6.104 Å) and finally to CdTe (6.481 Å). A cyclic annealing procedure was used during the growth of thick films, details of the anneal process parameters are described elsewhere [12, 13]. Figure 1(a) shows the XRD (422) rocking-curve scan of a 12 µm thick CdTe film. The low FWHM of 64 arcs indicates excellent crystal quality. Figure 1(b) shows the optical microscope image after a 30 s Everson etch of the same film. The low EPD value of $3x10^5$ cm^{-2} confirms the excellent crystal quality. These FWHM and EPD values are the best reported for MOVPE-grown CdTe on Si and equal to the state-of-the-art material obtained using MBE. Figure 1(c) shows the Everson EPD obtained for CdTe films of different thicknesses grown in this study. An exponential dependence of EPD on thickness is observed for thinner CdTe films, but the EPD appears to saturate for ~ 13 µm thick CdTe. This indicates that other dislocation reduction techniques like patterned growth or epitaxial lateral overgrowth (ELO) need to be used in combination with thick buffer layers and cyclic annealing in order to further reduce the EPD.

3.2 Patterned growth The patterned growth process involves selective homo-epitaxial growth of (211)B CdTe that does not wet the mask material. For this we used a 10 µm thick CdTe deposited by MBE on (211)Si substrate provided by NVESD. XRD θ-2θ scans (not shown here) confirm that the CdTe films grown on un-patterned MBE grown (211)B CdTe/Si substrates were single-crystal of (211) orientation. Growth was carried out in the temperature range from 275 ^{o}C to the 625 ^{o}C temperature range and selective nucleation of CdTe was established only in the growth window regions and not on the Si_3N_4 mask. This enables growth to begin in the window regions and then expand laterally over the mask. High temperatures and low pressures were found to be necessary to obtain good selectivity. Growth temperatures higher than 500 ^{o}C and reactor pressures lower than 25 Torr were found to be essential to obtain selectivity for the precursor mole fractions used (mole fraction of Te $\leq 10^{-3}$, mole fraction of Cd $\leq 6x10^{-4}$) and typical H_2 carrier flow rates in the 1.5 slm-2.5 slm range.

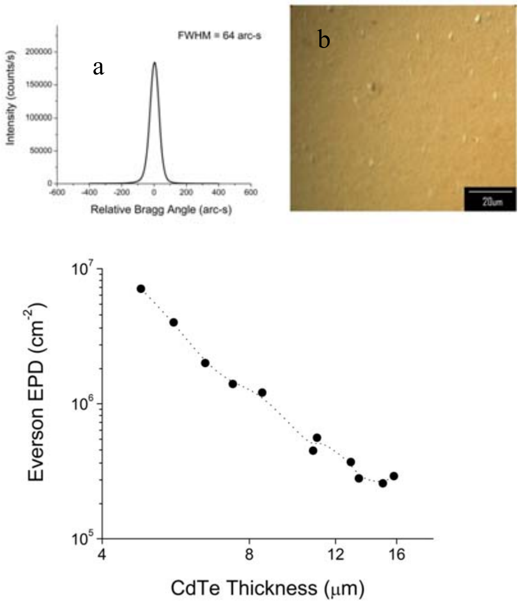

Figure 1 (a) XRD (422) rocking-curve scan of a 12 µm thick CdTe film. (b) Nomarski optical microscope image after a 30 s Everson etch of the same film. (c) Everson EPD obtained for CdTe films of different thicknesses grown in this study.

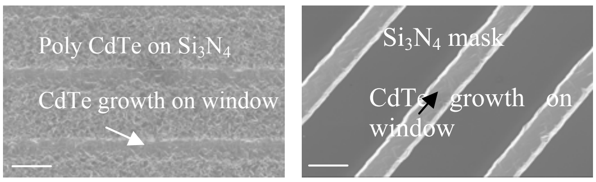

Figure 2 SEM images of CdTe growth on patterned Si_3N_4/CdTe/Si(211) substrates, (a) non-selectivity at growth temperature of 400 ^{o}C and reactor pressure of 100 Torr leading to polycrystalline growth on the mask, (b) good selectivity at 500 ^{o}C and 25 Torr. Marker represents 20 µm.

Figure 2(a) shows the surface of a CdTe film grown on a patterned substrate using the process parameters developed for blanket homo-epitaxial (211)B CdTe growth. Smooth CdTe surface is observed in the growth windows where the Si_3N_4 mask was etched to expose underlying CdTe. But non-selective nucleation leads to polycrystalline growth over the mask regions. Figure 2(b) shows good selectivity obtained (very little nucleation in the mask regions) using a higher growth temperature of 500 ^{o}C and lower reactor pressure of 25 Torr.

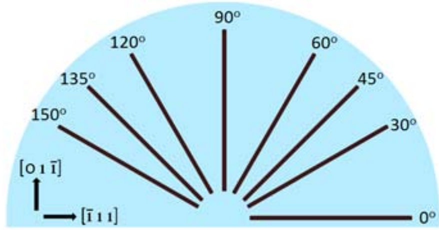

Figure 3 Schematic showing the orientation of the ELO stripes chosen for FIB SEM study from the circular pattern. Stripes on the mask were spaced 0.5^{o} apart.

The quality and surface morphology of ELO-CdTe have been shown to be very sensitive to the orientation of the growth windows [14]. So, choosing the right orientation for the stripe window is essential. The anisotropy during ELO was studied using a circular pattern consisting of 5 µm-wide growth windows arranged at 0.5^{o} angular intervals. The mask width varied from 15 µm in the center of the pattern to 40 µm towards the edge of the pattern. ELO using the circular-patterned substrates was conducted at 700 ^{o}C, reactor pressure of 25 Torr and DMCd and DETe mole fractions of $3.6x10^{-4}$ and $6.3x10^{-4}$, respectively. A scanning electron microscope (SEM) equipped with a focused ion beam (FIB) was then used to look at the cross-sections of the ELO-stripes. Figure 3 is a schematic showing the orientation of the ELO stripes chosen for the FIB-SEM study from this circular pattern. The orientation of the growth windows was measured with reference to the $[\bar{1}\,1\,1]$ direction, thus growth windows along $[\bar{1}\,1\,1]$ and $[0\,1\,\bar{1}]$ had 0^{o} and 90^{o} mis-orientations respectively with the $[\bar{1}\,1\,1]$ reference direction. Figure 4 shows the significant anisotropy observed in the geometry of the ELO stripes and the different facets obtained for ELO using growth windows along different orientations. ELO stripes with vertical side-walls and flat top-surfaces are desirable for future device fabrication. Our studies here show that this can be achieved using growth windows oriented along the $[0\,1\,\bar{1}]$ direction (90^{o} mis-orientation with the $[\bar{1}\,1\,1]$ reference direction]. Subsequent experiments were conducted using a parallel stripe pattern with growth windows along the $[0\,1\,\bar{1}]$ direction.

The ELO process time was next extended in order to ensure that growth from adjacent windows merged to form a continuous film. The rocking-curve FWHM increased from 85 arcs for the un-patterned (211)B CdTe/Si substrate to 184 arcs for the merged ELO film, indicating no improvement in crystal quality. The rough surface morphology of the ELO-grown CdTe precluded the use of Everson etch pit density characterization in order to estimate the TD density and compare it with the un-patterned starting substrates.

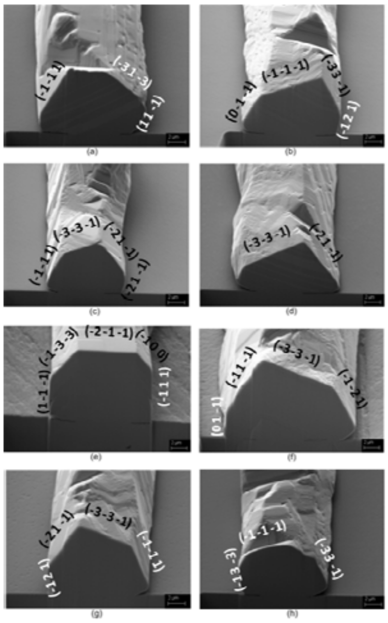

Figure 4 SEM images of ELO cross-sections (created using FIB milling) for growth windows with different mis-orientations with respect to the reference [$\bar{1}$ 1 1] direction: (a) 0^o, (b) 30^o, (c) 45^o, (d) 60^o, (e) 90^o, (f) 120^o, (g) 135^o, (h) 150^o. The ELO stripes display different facets depending on the orientation of the growth windows. Vertical side-walls and flat top-surfaces are only obtained for (e) 90^o mis-orientation with respect to [$\bar{1}$ 1 1] direction.

We speculate a couple of reasons for the poor quality of merged films. Since the mask region is very wide (40 µm), the selective growth process need to be carried out at high temperature (>500 ^{o}C) and at low pressure (<25 Torr). This is not an optimum temperature for the growth of films on blanket wafer. Also, since each stripe width is very large, over several microns, when the stripes merge, any small misorientation between the stripes will generate dislocations when they merge. This will result in higher X-ray FWHM. To overcome these difficulties, perhaps the patterning should be done on a nanometer scale. On a nanopatterned surface, the adjacent stripes are small in size and hence when merged may re-orient to get better quality films. Higher temperature annealing can be used to improve the layers as well. In addition, since the lateral width of the mask is narrow compared to the one used here, merged layers can be easily achieved even for (211)B CdTe, which has a high vertical growth rate compared with the lateral growth rate.

4 Conclusions

In conclusions, a MOVPE process was developed for growing excellent quality CdTe on (211)Si substrates using Ge and ZnTe interfacial layers. Use of TBAs exposure of Si and Ge layers was necessary to get (211)B oriented CdTe films. The best (211)B CdTe films grown in this study display a low X-ray diffraction (XRD) rocking-curve full-width-at-half-maximum (FWHM) of 64 arcs for a 12 µm thick layer and Everson etch pit density (EPD) of $3x10^5$ cm^{-2}. The MOVPE process parameters were next optimized for selective nucleation of CdTe on patterned (211)B CdTe with Si_3N_4 as a mask. High growth temperatures and low reactor pressure were necessary to ensure good selectivity. It is shown that vertical side-walls and flat top-surfaces were only obtained for growth windows along the [0 1 $\bar{1}$] direction. This stripe direction was used for growing merged CdTe layers on (211)B CdTe/Si substrates. The merged layers had higher X-ray FWHM compared to the layers grown on blanket wafers. The challenge posed by low aspect ratios (horizontal to vertical growth rate ratio) can be overcome by using nano-patterned starting substrates.

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